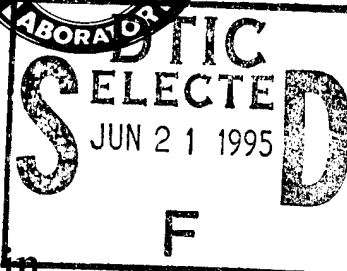




Environmental Effects of Dredging Technical Notes



Naturally Occurring Levels of Ammonia and Sulfide in Pore Water: An Assessment of the Literature

Purpose

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Ammonia and sulfide are natural constituents of sediment. Both are very toxic to aquatic organisms. Consequently, their presence may bias dredged material toxicity bioassays that are designed to evaluate the toxicity of persistent contaminants such as heavy metals and petroleum and chlorinated hydrocarbons. The purpose of this technical note is to summarize published information on sediment pore water ammonia and sulfide concentrations that occur in situ. In a subsequent technical note, this exposure information will be coupled with ammonia and sulfide toxicity data to estimate the potential influence of these constituents on dredged material toxicity bioassays.

Background

In aquatic ecosystems, ammonia is derived primarily via the hydrolysis of macromolecules and subsequent deamination of amino acids (Santschi and others 1990). The molecule exists in two forms, ionized (NH_4^+) and un-ionized (NH_3) ammonia (Wajsbrot and others 1990). Un-ionized ammonia appears to be the toxic moiety based primarily on studies with freshwater fish (Nimmo and others 1989). The proportion of total ammonia present in the un-ionized form increases with pH. For example, at pH values of 7, 8, and 9 (20 °C), the approximate percent of un-ionized ammonia is 0.4, 4.0, and 28 percent, respectively. Temperature and, to a lesser degree, ionic strength (that is, hardness or salinity) also affect the relative proportion of un-ionized ammonia (Emerson and others 1975; Thurston and others 1981; Williams, Green, and Pascoe 1986). Jones and Lee (1988) suggested that ammonia toxicity may be an important factor in many marine sediment bioassays. Ankley, Katko, and Arthur (1990) clearly demonstrated this for some freshwater sediments containing substantial amounts of anthropogenic chemicals. Ankley, Katko, and Arthur (1990) postulate that if ammonia is the causative agent in sediment toxicity bioassays, past

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interpretations regarding potential environmental impacts may have been erroneous.

Sulfides are compounds containing one or more sulfur atoms connected directly to a carbon, metal, and other nonoxygen atom. In sediments, sulfides exist as insoluble precipitates and as dissolved sulfide compounds. In the presence of oxygen, sulfide rapidly oxidizes to sulfate or, in some instances, to elemental sulfur (Ponnamperuma 1972). Sulfides, therefore, are usually associated with hypoxic or anoxic conditions such as may occur in highly organic and undisturbed sediments. H_2S , the toxicologically important form of sulfide, is produced when bacteria reduce sulfates and putrefy proteins.

Sulfides in pore water may be analyzed as total sulfides (TS), as dissolved sulfides (DS), and as H_2S . TS consist of acid-soluble metallic sulfides in suspended matter plus dissolved H_2S . DS remain after the suspended solids have been removed by flocculation and settling. H_2S may be analyzed directly or calculated from the concentration of DS, sample pH, and the ionization constant for H_2S (American Public Health Association (APHA) 1980). The relationship between H_2S and pH is opposite that for NH_3 . The proportion of H_2S in DS decreases with pH. For example, at pHs 6, 7, and 8, the approximate percent of H_2S is 90, 50, and 10 percent, respectively (APHA 1980). Since most sediments are near neutral (pH 7 to 8), the proportion of H_2S in DS is 10 to 50 percent. In contrast, H_2S represents only about 6 percent of DS in seawater (Bagarinao 1992).

Additional Information

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Procedure

In the literature examined, approximately 40 papers contained data on the levels of ammonia and sulfide in sediment pore water. The following information was extracted from each paper: range of ammonia and sulfide concentrations observed, method of pore water extraction, method of ammonia and sulfide analysis, pH, and depth of collection.

Most papers reported ammonia and sulfide concentrations on a molar basis. To be consistent, volume-specific concentrations (for example, milligrams per liter) were converted to molar equivalents using the conversions shown below. Also provided are useful relationships for converting back to volume-specific concentrations.

$1 \mu\text{M NH}_3 = 17 \mu\text{g NH}_3/\text{L}$
 $1 \mu\text{M NH}_4 = 18 \mu\text{g NH}_4/\text{L}$
 $1 \mu\text{M H}_2\text{S} = 34 \mu\text{g H}_2\text{S}/\text{L}$

$59 \mu\text{M NH}_3 = 1 \text{ ppm NH}_3/\text{L}$
 $56 \mu\text{M NH}_4 = 1 \text{ ppm NH}_4/\text{L}$
 $29 \mu\text{M H}_2\text{S} = 1 \text{ ppm H}_2\text{S}/\text{L}$

Results

Ammonia

Un-ionized ammonia (NH_3) was the most frequently reported ionic form (Table 1). Concentrations as high as $12,500 \mu\text{M}$ (430 ppm) were reported. Values between 10 and $1,000 \mu\text{M NH}_3$ (0.17 to 17 ppm) were more common, however. The most frequently used method for obtaining pore water was centrifugation (≈ 40 percent), followed by mechanical squeezer (≈ 30 percent). Autoanalyzer and ion-selective electrode were the first and second methods of choice for analyzing NH_3 . Kjeldahl distillation and indophenol spectrophotometric methods were used to analyze NH_4 . Most pore water samples were taken from depths ranging from 0 to 30 cm of sediment where pH values were near neutral (7.0 to 8.0).

Sulfides

H_2S concentrations as high as $10,000 \mu\text{M}$ (345 ppm) have been reported. However, values between 20 and $5,000 \mu\text{M}$ (0.7 to 170 ppm) were more common. The mechanical squeezer was the most frequently used method for obtaining pore water for sulfide analysis. Analytical methods included colorimetric, titration, and ion-specific electrode. Most pore water samples were taken from the upper 30 to 40 cm of sediment where pH values were near neutral.

Discussion

Reported concentrations of ammonia and sulfide in sediment interstitial water were highly variable. Factors contributing to this variability can be ranked. Probably the most important is geographic. The data reported in Tables 1 and 2 represent sediments and environments that vary greatly in their physicochemical properties and productivity, respectively.

The next most important factor contributing to the observed variability is probably seasonality. Sediment ammonia and sulfide levels are typically low in the winter and high in late spring and early fall (Berner 1980; Feijtel, DeLaune, and Patrick 1988; Howarth and Teal 1980; Howarth and others 1983). This seasonal cycle corresponds to the annual pattern of carbon fixation by

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Table 1. In Situ Concentrations of Ammonia in Sediment Pore Water					
Concentration Range, μM	Pore Water Removal Method	Method of Analysis	pH	Depth, cm	Citation
Ionic Form NH_3					
1,400-12,500	Dialysis sampler	Autoanalyzer	7.0-8.0	1-25	Boers and deBles 1991
0-6,320	Squeezer	Autoanalyzer	7.6-7.9	0-14	Murray, Grundmanis, and Smethie 1978
800-4,100	Centrifugation	Autoanalyzer	NR ¹	0-10	Klump and Martens 1981
130-3,235 ²	Centrifugation	Autoanalyzer	NR	NR	Brannon, Plumb, and Smith 1978
106-3,118 ²	Centrifugation	Ion-specific electrode	6.5-8.5	NR	Ankley, Katko, and Arthur 1990
2-1,500	Tube pressed into sediment	Ion-specific electrode	NR	0-8	Watson, Frickers, and Goodchild 1985
96-1,140	Dialysis sampler	Autoanalyzer	7.5-7.7	0-26	Viel and others 1991
110-1,540	Centrifugation	Autoanalyzer	7.0-7.9	0-30	Viel and others 1991
10-470	Centrifugation	Autoanalyzer	NR	0-10	Larat, Lasserre, and le Corre 1990
0-300	Squeezer	Ion-specific electrode	NR	0-40	Tisue, Edington, and Seils 1988
≈ 1 -126.7	Squeezer	Ion-specific electrode	7.6-8.6	NR	USDI 1992
24-35 ²	Squeezer	Autoanalyzer	6.9-7.4	2	Carr, Williams, and Fragata 1989
6-79	Dialysis sampler	NR	NR	198-594	Sly 1988
3-19 ²	Hand-suction pump	Autoanalyzer	NR	NR	Oliff and others 1970
≤ 1 -47	Centrifugation	Ion-specific electrode	NR	0-24	Simon 1989
0-30	Squeezer	Autoanalyzer	NR	0-30	van der Loeff 1980
¹ Not reported.					
² Concentration converted to micromoles per liter.					
(Continued)					

Table 1. (Concluded)

Concentration Range, μM	Pore Water Removal Method	Method of Analysis	pH	Depth, cm	Citation
Ionic Form NH_4^+					
5,000-200,000	Squeezer	Indophenol	NR	0-10	Raaphorst and others 1990
200-2,556 ²	Centrifugation	Kjeldahl distillation	NR	0-60	Brannon and others 1976
0-2,000	Squeezer	Kjeldahl distillation	NR	0-130	Rosenfeld 1981
20-1,310	Centrifugation	Kjeldahl distillation	NR	0-60	Sholkovitz 1973
38-735 ²	Filtration	Kjeldahl distillation	7.2-7.5	NR	Ho and Lane 1973
27-631	Squeezer	Kjeldahl distillation	6.9-7.6	0-18	Aller 1980
0-398	Centrifugation	NR	NR	0-40	Grasshoff 1976
0-18	Pipette sampler	Spectrophotometric	7.4-8.6	0-20	McLachlan 1978
$\leq 1-6$	Centrifugation	Indophenol	NR	0-9	Laima 1992

phytoplankton. Confounding this seasonal influence of primary production is the recent discovery that sediment ammonia exists in different exchangeable pools which also vary seasonally (Laima 1992).

Finally, two important contributors to the observed variability are inconsistent methods for both pore water removal and chemical analysis. Methods for these activities have been shown to greatly affect results (Howes 1985, Knezovich and Harrison 1987, Pittinger and others 1988). Among the studies reviewed in this survey, two of the most popular methods for obtaining pore water are centrifugation and mechanical squeezing. In a comparison of collection methods, Schults and others (1992) concluded that centrifugation was the most accurate and precise method for analysis of organic chemical contaminants in pore water. For H_2S , centrifugation should not violate the hypoxic integrity of the sample.

Summary

Literature was reviewed for sediment pore water concentrations of ammonia and sulfides. Toxic constituents of concern are un-ionized ammonia (NH_3) and hydrogen sulfide (H_2S). Concentrations of NH_3 as high as 12,500 μM (430 ppm) have been reported. However, values between 10 and 1,000 μM (0.17 to 17 ppm) are more common. The highest concentration of H_2S was about 10,000 μM (345 ppm). Most values ranged between 20 and 5,000 μM (0.7 to 170 ppm). Factors contributing to the variable pore water concentrations

Table 2. In Situ Concentrations of Sulfides in Sediment Pore Water					
Concentration Range, μM	Pore Water Removal Method	Method of Analysis	pH	Depth, cm	Citation
Ionic Form H_2S					
0-10,080	Squeezer	Colorimetric	7.6-7.9	0-140	Murray, Grundmanis, and Smethie 1978
0-5,882 ¹	Centrifugation	Colorimetric	NR ²	0-140	Moore and Dillon 1993
0-4,920	Squeezer	Titration	6.1-7.2	0-54	Boulegue, Lord, and Church 1982
3-255	Centrifugation	Colorimetric	NR	1-16	Swider and Mackin 1989
22-287	Squeezer	NR	NR	7-24	Aller 1980
0-3 ¹	Pipette sampler	Spectrophotometric	7.4-8.6	0-20	McLachlan 1978
<2.9 ¹	Filtration	NR	6.8-7.6	0-60	USACE 1975
Dissolved Sulfides					
5-50	Squeezer	Measured on precipitated ZnS	NR	0-10	Fossing and Jorgensen 1990
0-1	Squeezer	Colorimetric	4.1-7.2	5-20	Howarth and others 1983
0-2,900	Squeezer	Titration	7.0-9.0	0-80	Krom and Sholkovitz 1977
Total Sulfides					
0-212	Squeezer and in situ sampler	NR	NR	2-20	Howes 1985
0-5 ¹	Squeezer	Ion-specific electrode	7.7-7.8	1-45	Brooks, Presley, and Kaplan 1968
0- ≤ 1	Squeezer	Ion-specific electrode	7.6-8.6	NR	USDI 1992
¹ Concentration converted to micromoles per liter.					
² Not reported.					

include geographic dissimilarities, seasonal effects, different chemical methods for analyzing ammonia and sulfide, and variable techniques for obtaining pore water. Centrifugation is the method of choice for obtaining interstitial water from dredged material samples.

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